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# Fixed-Fugacity Option for the EQ6 Geochemical Reaction Path Code

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December 20, 1984

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## Contents

Abstract .....	1
1. Introduction .....	2
2. Fixed-Fugacity Model .....	4
3. Program Modifications, Change Levels, and Limitations .....	5
4. Sample Problems—Albite Dissolution at Fixed Fugacities of CO <sub>2</sub> .....	7
References .....	10
Appendix A. Glossary of Major Variables .....	11
Appendix B. Summary of INPUT File Changes .....	13
Appendix C. Sample INPUT File .....	15
Appendix D. Subroutine NLKFFG Listing .....	19

# **Fixed-Fugacity Option for the EQ6 Geochemical Reaction Path Code**

## **Abstract**

EQ3/6 is a software package used to model aqueous geochemical systems. The EQ6 code allows reaction paths of dynamic systems to be calculated. This report describes a new option for the EQ6 computer program that permits the fugacity of any gas in the EQ6 data base to be set to a fixed value. This capability permits simulation of the effect of rapid chemical exchange with a large external gas reservoir by allowing the user to fix the fugacities of selected gas species. Geochemical environments such as groundwater systems open to the atmosphere (e.g., the unsaturated zone), natural aqueous systems that form closed systems at depth, and experimental systems that use controlled atmospheres can be modeled. Two of the principal geochemical weathering agents,  $\text{CO}_2$  and  $\text{O}_2$ , are the most likely gas species for which this type of exchange may be important. An example of the effect of constant  $\text{CO}_2$  fugacity on both open and closed systems is shown for the case of albite dissolution ( $\text{NaAlSi}_3\text{O}_8$ ) in distilled water. This example demonstrates that the effects of imposed fugacities on geochemical systems can be considerable.

# 1. Introduction

The Nevada Nuclear Waste Storage Investigations (NNWSI) Project is part of the U.S. Department of Energy's Civilian Radioactive Waste Management (CRWM) Program. The EQ3/6 Modeling Task of the NNWSI Project involves modifying the capabilities of the EQ3/6 geochemical codes to meet the geochemical modeling needs of the NNWSI project. EQ3/6 will be used to model the complex chemical processes between groundwater and the repository host rock, and to evaluate the geochemical effects of the potential migration of radionuclides to the water table and into the accessible environment. The potential repository horizon is a welded-devitrified tuff located beneath Yucca Mountain and situated above the water table in the unsaturated zone (Vieth, 1982). This document describes a capability that has been added to the EQ6 code that permits the evaluation of chemical reactions occurring in the unsaturated zone. Since oxidizing conditions are expected in the unsaturated zone at Yucca Mountain (Roseboom, 1983; Wollenberg et al., 1983), the exchange of  $O_2$  and  $CO_2$  should be especially significant. The unsaturated zone can be conceptualized as a large external reservoir containing  $O_2$  and  $CO_2$  at fixed fugacities. As these gases are consumed by reactions in the waste-package environment, they are continually replenished by this reservoir.

The EQ6 computer code is a part of the EQ3/6 software package (Wolery, 1979, 1983, 1984a, 1984b). This program can be used to compute models of the evolution of aqueous geochemical systems (such evolution is often termed a reaction path). Calculations of this kind have been carried out mostly for systems that are effectively closed, where rapid exchange with gas reservoirs does not occur. Incorporating the fixed-fugacity option into the EQ3/6 package will permit more rigorous geochemical investigation of various hydrologic regimes, including correlation with relevant laboratory experiments.

Dissolved gas species such as  $O_2$ ,  $CO_2$ , and  $CH_4$  may be produced or consumed during reactions of aqueous solutions with minerals, solids, and organic matter in aqueous geochemical systems. For a gas phase, equilibrium with an aqueous solution is expressed in terms of fugacity although its actual composition is reported in terms of partial pressure. A specific fugacity is defined for each such gas species in the aqueous phase. The partial pressure (p) of each species is related

to the fugacity (f) by the fugacity coefficient ( $\chi$ ) where

$$f = \chi p \quad (1)$$

Redlich and Kwong (1949) and Flowers (1979) discuss methods of estimating fugacity coefficients. For the following discussion, the reader can assume a fugacity coefficient of unity and equate fugacity with partial pressure. In EQ6 the fixed-fugacity option requires input fugacities measured in bars. A bar is nearly equivalent to one atmosphere (1 atm = 1.013 bar).

Exchange between a gas phase and an aqueous solution is driven by the difference in the fugacities of the two phases, assuming that the exchange is isothermal. If the concentration of the species in the gas phase is large compared to the concentration in the aqueous system, then the fugacity of the gas phase controls the fugacity of the species in the aqueous system provided the concentration in the gas phase can be rapidly replenished. Imposing such constraints on a geochemical system can significantly alter the paths and rates of chemical reactions in an aqueous system.

The concentration of carbon dioxide in oxygenated groundwaters in equilibrium with atmospheric  $CO_2$  levels is commonly found to be approximately  $10^{-3.5}$  atm at 25°C. The partial pressure of  $CO_2$  in natural waters can be greater than atmospheric when processes, such as the biochemical oxidation of organic carbon, and/or dissolution of carbonate-rich rocks are significant. For example, groundwater in equilibrium with pure calcite at 25°C can usually be approximated by a  $CO_2$  partial pressure of  $10^{-2}$  atm, and values in soil waters may range from  $10^{-3}$  to  $10^{-1}$  atm (Freeze and Cherry, 1979). Waters constrained to maintain a constant partial pressure of  $CO_2$  for computational purposes may represent both open and closed systems and provide necessary conditions to model a variety of geochemical environments.

The modeling of experimental laboratory results is also an important EQ3/6 application for the NNWSI Project. Laboratory apparatus are often set up with controlled atmospheres. These types of experiments are performed by bubbling a gas phase through the sample chamber to maintain saturation. For example, Busenberg and Clemency (1976) and Busenberg (1978) investigated the dissolution kinetics of feldspars at 25°C

and 1 atm  $\text{CO}_2$  partial pressure in a one-liter reaction vessel. The presence of the gas phase is used to avoid feldspar saturation from being reached.

The system was saturated with water vapor to keep the apparatus from drying out.

## 2. Fixed-Fugacity Model

The fixed-fugacity option (NFFG) permits the user to fix the fugacity of any gas species in the data base to a constant value. This allows the following types of systems to be modeled: (1) systems open to the atmosphere, (2) closed systems that may be representative of equilibrium with a particular mineral phase at a specified temperature, or (3) conditions of laboratory reaction vessels. More than one such gas species can be fixed in a single run. The user specifies the fugacity that is to be maintained. The fugacity of a particular species is actually fixed by creating a fictive solid phase within the EQ6 run for each specified gas, and equilibrium is maintained between the solid and gas phases. Each fictive solid phase is also in equilibrium with the aqueous solution, which allows the solid-gas equilibrium to represent the fugacity. The log of the fixed-fugacity value is substituted for the equilibrium constant for that reaction pair. The solid phase is internally constructed with each run. The external data base is not affected. This method ensures that fixed fugacities are used only when they are desired.

Carbon dioxide is used to illustrate the solid-gas-equilibrium relationship. The reaction between solid and gaseous forms may be written

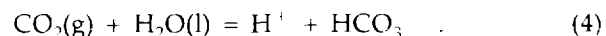


The corresponding mass action equation is

$$\log f_{\text{CO}_2} = \log K_2 \quad (3)$$

Thus, by creating a fictive mineral or solid phase and fixing the equilibrium constant for Eq. (2), the desired fugacity will be maintained as long as the aqueous solution remains in equilibrium with the fictive solid phase  $\text{CO}_2(\text{s})$ . When the gas phase is considered together with the solid in the aqueous phase, they simultaneously influence the composition of the overall solution.

The EQ3/6 data base stores a dissolution reaction for each gas species. For  $\text{CO}_2$ , the reaction is

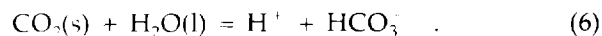


The corresponding mass action equation is

$$\log (a_{\text{H}^+}) + (\log a_{\text{HCO}_3^-}) - (\log f_{\text{CO}_2}) - (\log a_w) = \log K_4 \quad (5)$$

$\log K_4$  is stored in the EQ3/6 data file.

The parallel reaction for the dissolution of the corresponding fictive solid would be



The corresponding mass action equation is

$$\log (a_{\text{H}^+}) + (\log a_{\text{HCO}_3^-}) - (\log a_w) = \log K_6 \quad (7)$$

The difference between Eqs. (6) and (4) yields Eq. (2). Similarly, subtracting Eq. (5) from Eq. (7) yields

$$\log K_6 = \log K_4 + \log f_{\text{CO}_2} \quad (8)$$

The fictive mineral is constructed in the code by incrementing the mineral array by one and copying the gas dissolution reaction coefficients into the array for mineral dissolution reactions for the new phase [i.e., Eq. (6) is a transformation of Eq. (4)]. The equilibrium constant for the fictive solid is calculated from Eq. (8).

The fugacity is fixed at the desired value only if the corresponding fictive solid appears in the model system in equilibrium with the aqueous solution. There must be enough of the gas component present in the system to achieve saturation. The mass of the fictive solid is specified on the input file and represents the actual mass of the gas in the controlling atmosphere. If it does not exist or becomes exhausted, the actual fugacity in the aqueous system may fall below the desired value. In some situations the gas component may be produced in the aqueous system and additional fictive solid may form. For example,  $\text{CO}_2$  is produced by the process of the decomposition of organic matter. In most weathering environments, by contrast, if the gas components  $\text{CO}_2$  and  $\text{O}_2$  are consumed, the masses of corresponding fictive solids would decrease.



### 3. Program Modifications, Change Levels, and Limitations

The number of fixed-fugacity gas species is indicated by the NFFG parameter on the EQ6 INPUT file (See Appendices B and C). Following this line, NFFG lines are inserted specifying the name of a gaseous species (UFFG), the number of moles, if any, of the gas to add to the system at the start of the run (MOFFG), and the logarithm of the desired fugacity (XLKFFG). The user controls the size of the external gas reservoir by the MOFFG parameter. In order to ensure fixing a species' fugacity, EQ6 allows the user to add the mass of this species to the system, forcing saturation and providing some control over the size of the reservoir. The user should monitor the fugacity behavior in a run to see if exhaustion of the specified phase occurs. This is done by setting IOPR8 = 1, causing a printout of the independently calculated gas fugacities (FUG) and their logarithms (FUGLG).

The fixed fugacity option exists at three levels in EQ6, and limitations on usage vary with each level. At the first level, corresponding to EQ6.3230U21 (released April 4, 1984, as part of version 3230B), the changes consist of the addition of one new subroutine, NLKFFG, and changes to the main program and subroutines READZ, INDATZ, SCRIBE, and SHIFT. An abbreviated summary of these changes is given below:

1. The maximum number of fixed-fugacity species (NFFGMX) allowed by the code is set in MAIN.

2. Subroutine READZ is modified to read the additional NFFG, UFFG, MOFFG, and XLKFFG parameters from the input file.

3. Supplementary data files DATA2 and DATA3 are read in subroutine INDATZ and then decoded into mineral, aqueous species, gas and solid solution arrays. If any fixed-fugacity phases have been specified (NFFG > 0), subroutine INDATZ calls a new subroutine, NLKFFG.

4. New subroutine NLKFFG (Appendix D) isolates the gas species having a fixed fugacity, and creates an internal companion solid phase for each such species. This new phase is identified on output files with the same gas species name preceded by the label "FIX." The internal counter variable, NMT, is incremented by NFFG phases and the thermodynamic values for the gaseous species are transferred into the mineral arrays for the newly constructed solid phase. The log K of the new solid phase is modified [according to Eq. (8)] so that the equilibrium between the gaseous and solid phases maintains the specified fixed-fugacity value, XLKFFG.

5. Normal action of subroutine SHIFT is bypassed for all fixed-fugacity phases. Fixed-fugacity phases are prefixed by "FIX" as the first word of the three word name in the code. In order to maintain the fixed-fugacity value, saturation must be maintained through equilibrium between the solid and gaseous components described above. The normal function of SHIFT would upset this balance by removing mass from the system.

6. Subroutine SCRIBE, which writes the PICKUP file, is modified to write the NFFG, UFFG, MOFFG, and XLKFFG parameters consistent with the changes to READZ. (The PICKUP file is an INPUT file for continuing the reaction-path calculation.)

Problems were discovered in the coding at this change level that resulted in unanticipated second-order effects. First, fixed-fugacity phases could be inadvertently suppressed by the subset-selection-suppression options associated with the NXOPT parameter on the INPUT file. If such phases are suppressed, the fixed-fugacity option is effectively negated unless the phase is specified as an exception (Wolery, 1984b). A similar problem could arise from the NXMOD alter/suppress options. This is unlikely to occur by accident, because phases affected by these options must be individually specified on the INPUT file. The NXMOD options should not be specified for fixed-fugacity phases. In this version of the code, EQ6.3230U21, "CALL NLKFFG" preceded "CALL ALTERZ," hence if one altered the thermodynamic data for a gas, such as "CO<sub>2</sub>(G)," the thermodynamic parameters for the corresponding fictive mineral, "FIX\_\_\_CO<sub>2</sub>(G)," would not reflect the change, and the fugacity would not be fixed at the specified value.

It may be useful to use a fixed-fugacity mineral as a reactant. This allows gradual addition of the gas component to the system, as opposed to the initial one-shot addition via the MOFFG parameter. In the 3230 versions of EQ6, it was observed that the initial thermodynamic calculations occasionally failed for high MOFFG values (e.g., for CO<sub>2</sub>, with MOFFG = 0.5 mole). An obvious way to get around this difficulty is to execute a preliminary run to add the mass of gas gradually. In this version of the code "CALL GLXRN," which decodes reactant names, and "CALL INNDX," which decodes the names of the species in the component matrix, preceded "CALL NLKFFG" in subroutine INDATZ. Hence subroutines GLXRN and INNDX would fail to find a

mineral such as "FIX\_\_CO<sub>2</sub>(G)" in the mineral array because they were not yet added by "CALL NLKFFG," and the subroutines would flag the incident as a name match error.

The original fixed-fugacity modification did not allow for the possibility of a sequence of runs in which fugacities were fixed in some segments, and not in following ones. No provision had been included to eliminate fixed-fugacity phases at the start of a subsequent run segment.

The following changes brought EQ6.3230U21 up to the second-change level, EQ6.3230U25.

1. Subroutine FLGSTZ was changed so no NXOPT option suppresses any mineral beginning with "FIX\_\_."

2. Subroutines SUPPRZ and ALTERZ were changed so no NXMOD option suppresses or alters the thermodynamic data for any mineral beginning with "FIX\_\_."

3. In the subroutine INDATZ, "CALL NLKFFG" was moved down several lines, past the point at which solid solution thermodynamic parameters (APX) are read. Then "CALL ALTERZ" was moved up to immediately precede "CALL NLKFFG." The block of coding between "IF (QRDATZ) GO TO 3072" and "3072 CONTINUE," which includes "CALL GLXRN" and "CALL INNDX" was moved to after "CALL NLKFFG."

4. In subroutines READZ and SCRIBE, the position of the NFFG option on the INPUT/PICKUP file was moved to the top half of the file, just after the NXOPT option.

5. In subroutine SHIFT, minerals beginning with "FIX\_\_" are protected only if NMODL1 = 3 (flow-through open system mode).

These changes address all the problems in the first-change level. In order to go from a run segment in which a fugacity is fixed for a particular phase to one in which it is not, the user must execute an intermediate run. An additional option was added to the input file, IOPT5 = 2; this eliminates all pure minerals in equilibrium with the aqueous system, both fictive and real. This inter-

mediate run must be made with the KSTPMX option set equal to zero (this tells the code not to make any steps) and NMODL1 set not equal to three. This method is awkward because one may desire to retain some of the fictive and real minerals. The fictive minerals can be retained by including them on the INPUT file for subsequent runs by specifying their masses with the MOFFG parameter. Non-fictive minerals can similarly be restored by declaring them active reactants (JREAC = 0) and by specifying the masses with the MORR parameter, and rate constants yielding positive dissolution rates. All such equilibrium minerals will be put back into the component matrix upon the first call to subroutine NEWTON.

The third-change level, embodied in EQ6.3245C36 (expected to be released in early 1985) avoids this clumsiness. Subroutine INNDX flags any minerals that are in the input component matrix, but which are not specified under the current NFFG input. Subroutine INDATZ then loads such minerals into the mineral array using a special call to subroutine NLKFFG, which is now called separately for each gas. Each left over fixed-fugacity mineral so identified is thermodynamically suppressed, and the fugacity is not fixed. INDATZ then purges these phases from the matrix and recalculates the mass totals of the components (elements) in the remaining aqueous system. The run then proceeds in the usual manner. The mass-total recalculation required that MTEAQ, the mass of each component in aqueous solution, be added to the INPUT/PICKUP file. This allows the recalculation to proceed by adding the contributions for the phases remaining in the system. Recalculation by subtraction would be much simpler but is avoided because it is generally less accurate, and because it could be fatally inaccurate if the total mass of a component in the system were only from fixed-fugacity minerals. Enhanced numerics also make it unlikely that the code will fail by adding large gas masses through the MOFFG input parameter.

#### 4. Sample Problems—Albite Dissolution at Fixed Fugacities of CO<sub>2</sub>

The EQ6 code was used to simulate the dissolution of pure albite (NaAlSi<sub>3</sub>O<sub>8</sub>) in distilled water at 25°C for various CO<sub>2</sub> partial pressures. The initial system was taken to be saturated with CO<sub>2</sub> at a normal atmospheric level (10<sup>-3.5</sup> atm). The sample problems include the case of free drift (case 1), where the fugacity of CO<sub>2</sub> is not constant, and fixed-fugacity cases for 10<sup>-3.5</sup>, 10<sup>-2</sup>, and 1.0 bar (cases 2, 3, and 4). The latter three cases are representative of solutions with controlled CO<sub>2</sub> partial pressure ranging from atmospheric to 1 bar, which is often created in laboratory experiments by bubbling carbon dioxide through a closed reaction vessel.

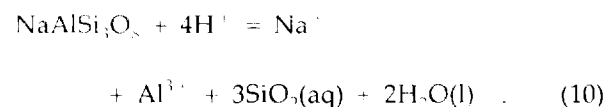
To assess the effect of fixing the fugacity of CO<sub>2</sub> on the kinetics of the reaction, the dissolution rate of the albite was represented by

$$d\xi/dt = ksf[1 - e^{-A/\sigma RT}] \quad (9)$$

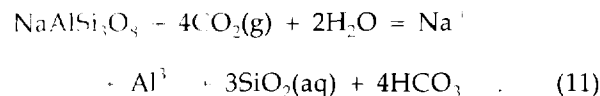
where  $\xi$  is the reaction progress variable, which is equivalent to the number of moles of albite ( $n$ ) dissolved ( $d\xi/dt = -dn/dt$ ),  $t$  (sec) is unit time,  $k$  ( $3.7 \times 10^{-17}$  mol/cm<sup>2</sup>-s) is the rate constant,  $s$  (10<sup>5</sup> cm<sup>2</sup>) is the surface area,  $f$  (assumed to be unity) is the ratio of effective to total surface area,  $A$  is the thermodynamic affinity driving the reaction,  $\sigma$  is a stoichiometric adjustment factor (assumed to be unity),  $R$  is the gas constant, and  $T$  is the absolute temperature. Assuming one kilogram of distilled water, the rate constant for albite was calculated from the experimental data of Knauss and Wolery (1985). For a discussion of the nature and origin of this equation, see Aagaard and Helgeson (1982).

A complete input file for the case of CO<sub>2</sub> fugacity fixed at 10<sup>-3.5</sup> bar appears in Appendix B. The lower part of the input file labeled "PICKUP" was created by EQ3NR (Wolery, 1983) for a solution initially equilibrated at 25°C with atmospheric CO<sub>2</sub> and with a pH consistent with electrical balance. This solution composition is probably a realistic representation for samples of distilled H<sub>2</sub>O used in laboratory experiments.

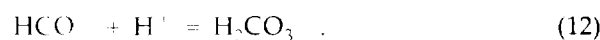
In CO<sub>2</sub>-H<sub>2</sub>O solutions, the amount of solid that dissolves depends on the partial pressure of CO<sub>2</sub>. The hydrolysis of feldspar in pure water can be represented as



In CO<sub>2</sub>-H<sub>2</sub>O solutions, the net reaction for the hydrolysis of feldspar can be described by combining Reactions 4 and 10 to yield



The presence of carbon dioxide in solution increases the amount of feldspar that a solution can dissolve. The formation of bicarbonate ion, caused by dissociation in CO<sub>2</sub>-H<sub>2</sub>O solutions, causes more feldspar to be hydrolyzed [Eq. (11)] than would be found in pure water [Eq. (10)]. This effect can be further complicated by the neutralization of the bicarbonate ion to carbonic acid,



The neutralization can be seen in the case of free drift where the carbon dioxide is consumed as the reaction proceeds and the fugacity of CO<sub>2</sub> drops several orders of magnitude, while a significant amount of carbonic acid is formed (Fig. 1). Conversely, in the other cases, an amount of solid CO<sub>2</sub> is consumed to keep the fugacity at a constant value (Fig. 2). In the last two cases,  $f = 10^{-2}$  and  $f = 1$ , the specified constant fugacities are much greater than the initial concentration of CO<sub>2</sub> available and require some of the fictive solid to be instantaneously consumed at the start of the run to bring the fugacity up to the desired concentrations. Initial consumption for cases three and four is  $3.25 \times 10^{-4}$  and  $3.27 \times 10^{-2}$  moles of CO<sub>2</sub>, respectively.

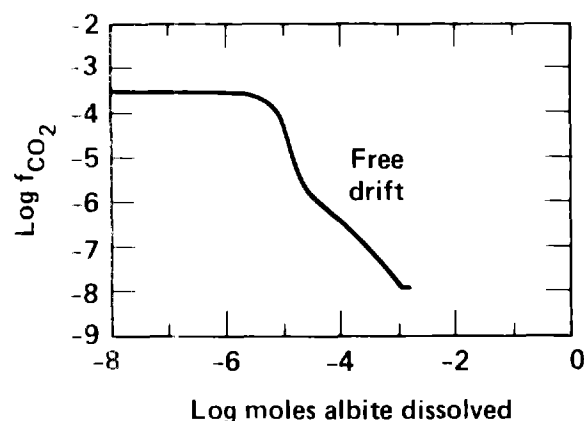


Figure 1. The fugacity of CO<sub>2</sub> in the free drift run (case 1).

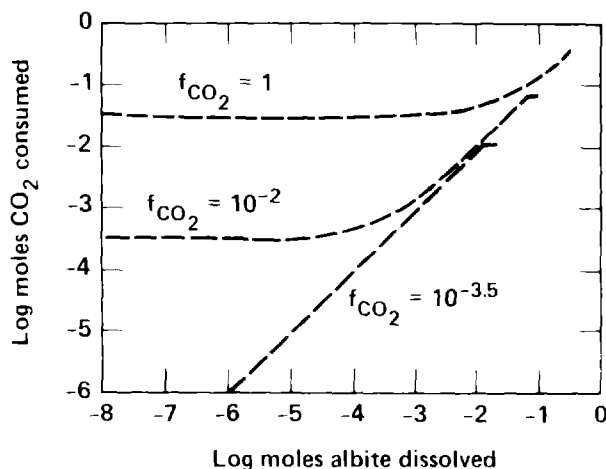


Figure 2. Consumption of  $\text{CO}_2$  in the fixed fugacity runs at  $10^{-3.5}$ ,  $10^{-2}$ , and 1 bar (cases 2, 3, and 4).

At higher  $\text{CO}_2$  fugacities, more albite must dissolve to reach saturation ( $A = 0$ ), as shown in Fig. 3. This is expected because, as  $\text{CO}_2$  is added to maintain the higher fugacities, more acid is created. This is also apparent in Fig. 4, which shows the extent of reaction progress with time. The leveling off of these curves indicates a close approach to saturation, with progressively greater amounts of albite being dissolved. The time required to actually reach saturation is infinite, a result of the rate law chosen in EQ6 [given by Eq. (9)].

The effect of fixed  $\text{CO}_2$  fugacities on pH in the course of the reaction is shown in Figs. 5

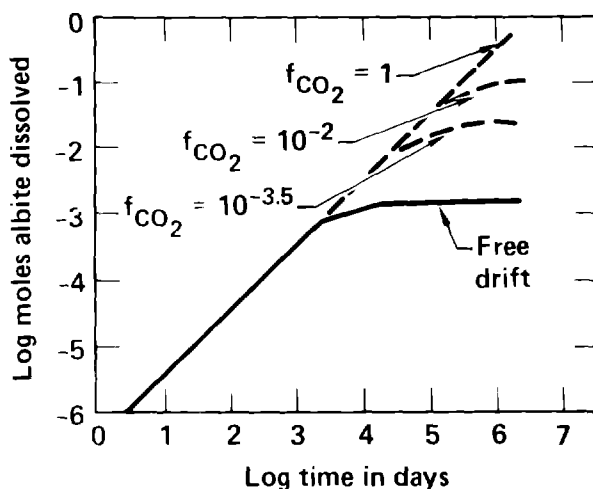


Figure 4. The extent of reaction progress as a function of time for the four cases discussed in the text.

and 6. The pH values decrease with increasing fugacities, as is expected, because more  $\text{CO}_2$  is required to maintain higher fugacities. This effectively delays the rise in pH that occurs because of feldspar hydrolysis. The pH values near saturation in each case are also lower at the higher fugacities.

In the first three cases (free drift and fixed fugacities of  $10^{-3.5}$  and  $10^{-2}$ ), the sequence of secondary mineral formation is gibbsite [ $\text{Al}(\text{OH})_3$ ], kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ], quartz [ $\text{SiO}_2$ ], and paragonite [ $\text{NaAl}_2(\text{AlSi}_3\text{O}_8)(\text{OH})_2$ ]. Gibbsite is quickly consumed after kaolinite appears because

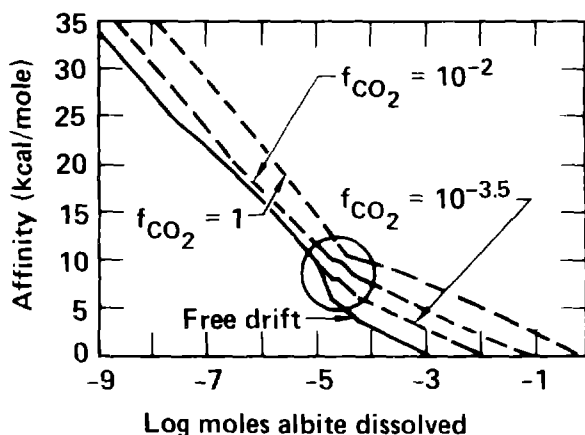


Figure 3. The affinity (thermodynamic driving force) for albite dissolution as a function of reaction progress for the four cases discussed in the text. The region within the circle has not been dashed, to preserve actual curvature.

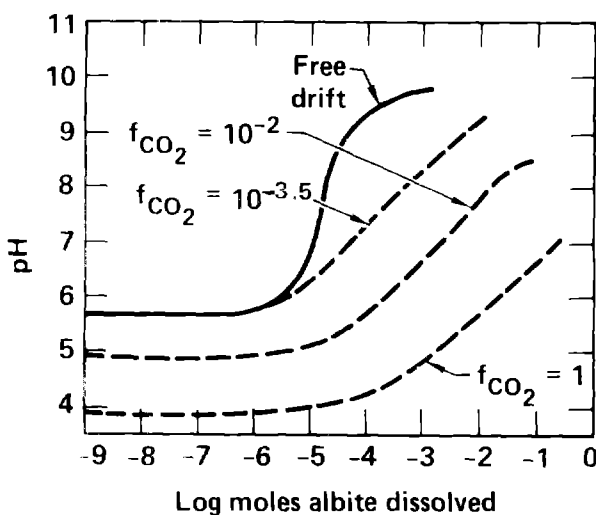


Figure 5. The pH as a function of reaction progress for the four cases discussed in the text.

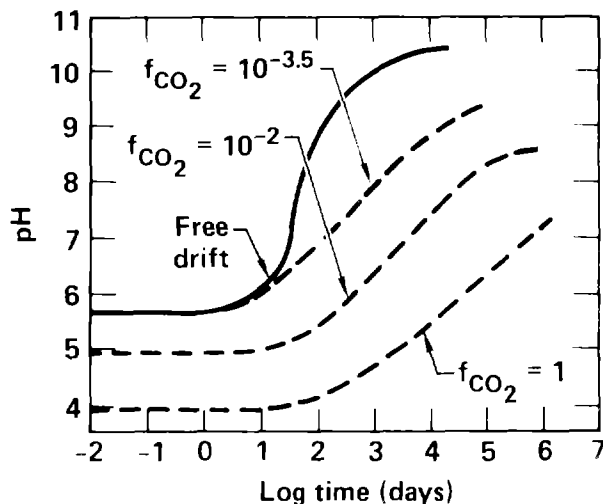


Figure 6. The pH as a function of time for the four cases discussed in the text.

of the mutual competition for aluminum. Kaolinite is similarly consumed after appearance of paragonite (Fig. 7). With increasing  $\text{CO}_2$ , gibbsite does not appear and quartz and kaolinite dominate the product assemblage (Fig. 8). More of the secondary reaction products are formed at higher  $\text{CO}_2$  fugacities, which is expected because more of the albite dissolves.

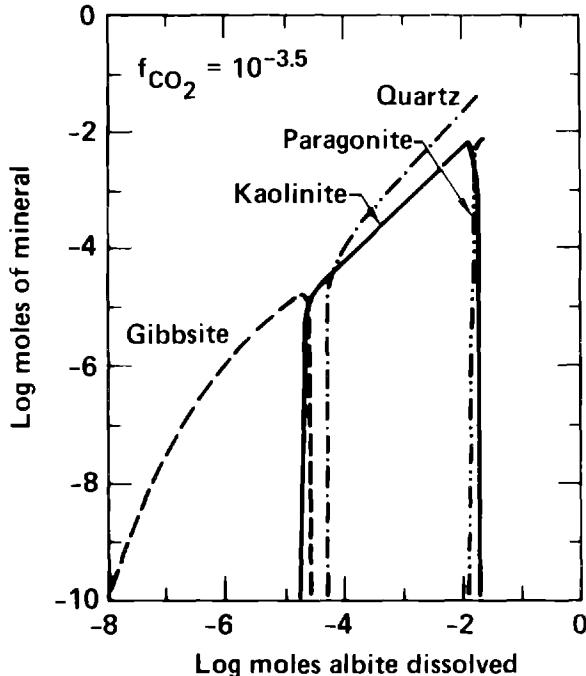


Figure 7. The masses of product minerals as a function of reaction progress for the case of  $\text{CO}_2$  fugacity fixed at  $10^{-3.5}$  bar.

The secondary phases that formed in these runs were those that are thermodynamically most stable according to the data base but this does not always result in the most realistic models. For example, a clay of roughly the composition of sodium montmorillonite is a more likely product than paragonite. Similarly, a solution may become supersaturated with respect to a phase, such as quartz, rather than precipitating the phase upon reaching saturation. Given these considerations, the cases above have shown that the influence of constant fugacities on reacting aqueous geochemical systems may be considerable.

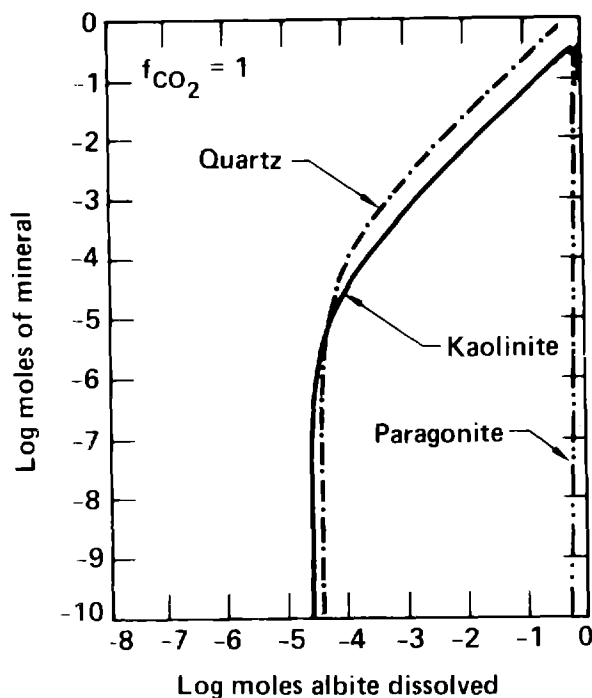


Figure 8. The masses of product minerals as a function of reaction progress for the case of  $\text{CO}_2$  fugacity fixed at 1 bar.

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## Appendix A. Glossary of Major Variables

AGS	Array of coefficients used to calculate XLKG as a function of temperature.
AMN	Array of coefficients used to calculate XLKM as a function of temperature.
CDRG	Array of coefficients for a gas-dissolution reaction.
CDRM	Array of coefficients for a mineral-dissolution reaction.
CEGS	Array of stoichiometric coefficients for a gas.
CEMN	Array of stoichiometric coefficients for a mineral.
FUG	The calculated fugacity of a gas species.
FUGLG	The logarithm of the calculated fugacity of a gas species.
IOPR8	Option switch to print the calculated equilibrium fugacities (FUG) and their logarithms (FUGLG) of the various gas species read into memory.
MOFFG	Number of moles of the gas species specified by UFFG to be added to the system at the start of the run.
MTE	The number of moles of an element in the aqueous system.
MTES	The number of moles of an element in the aqueous system at the previous point of reaction progress.
MWTGS	Molecular weight of a gas species.
MWTMN	Molecular weight of a mineral.
NFFG	Number of gas species with imposed fixed fugacity.
NFFGMX	Maximum number of fixed-fugacity species allowed by EQ6 (the dimensioned limit).
NGT	Total number of gas species read into memory from the data file.
NMT	Total number of minerals read into memory from the data file; extended to include fictive solids that correspond to gases whose fugacities are to be fixed.
NMTMAX	The dimensioned limit of the number of minerals in memory.
UFFG	Name of a gas species whose fugacity is to be fixed.
UGAS	Name of a gas species.
UMIN	Name of a mineral.
XLKFFG	The logarithm of the fugacity to be imposed on the species designated by UFFG.

XLKG	The logarithm of the equilibrium constant for a gas-dissolution reaction.
XLKM	The logarithm of the equilibrium constant for a mineral-dissolution reaction.



## Appendix B. Summary of INPUT File Changes

In order to run EQ3/6 with the fixed-fugacity option, the INPUT file must be modified in the following way (for the second- and third-change levels):

1. Insert the NFFG parameter after NXOPEX or NXOPT if NXOPEX = 0 (see below) in the upper part of the EQ6 INPUT file. If NFFG = 0, insert this line and all previous INPUT files should run correctly.
2. If NFFG > 0, then 1 to NFFG records must be inserted after the NFFG line, indicating the species name UFFG, moles of the species to add to the system MOFFG, and the desired log fugacity value XLKFFG.

The new input lines are shown below as they fit in between previously existing input lines on the INPUT file for the 3245 version of EQ6:

-----	
NXOPT	( 12X, I2 )
For N =1 to NXOPT:	
(UXOPT(N), UXCAT(J,N), J=1,2)	( 12X, A6, 1X, 2A6 )
 NXOPEX	 ( 12X, I2 )
For N =1 to NXOPEX:	
(UXOPEX(J,N), J=1,2)	( 12X, 2A6 )
-----	
NFFG	( 12X, I2 )
For N =1 to NFFG:	
(UFFG(J,N), J=1,2)	( 12X, 2A6,
MOFFG(N), XLKFFG(N)	11X, E12.5, 12X, E12.5 )
-----	
NRCT	( 12X, I2 )
For NRC=1 to NRCT:	
(UREAC(J,NRC), J=1,3)	( 12X, 3A6 )
JCODE(NRC), JREAD(NRC)	( 12X, I2, 10X, I2 )
MORR(NRC), MODR(NRC)	( 2( 12X, E12.5 ) )

Wolery (1984b) gives full discussion of the INPUT file for the 3245 version of EQ6. The location of the NFFG parameter above has been changed from the 3230 version of EQ6 where the associated additional lines were located in the lower half of the EQ6 INPUT file. This change eliminates the need for EQ3NR to write the NFFG value on the PICKUP file and allows the user to construct all EQ6 input independently of the PICKUP file.



## Appendix C. Sample INPUT File

This is the INPUT file for the run with the CO<sub>2</sub> fugacity fixed at 10<sup>-3.5</sup> bar. The file itself, as shown, is all lower case. The part of the file beginning with "input file: idw01a" is the PICKUP file written by EQ3NR.

---

```

1 input file name: ialbs01      revised 03/05/84
2
3 the dissolution of albite at 25 deg c with a fugacity of co2 in
4 equilibrium with atmospheric levels (log pco2 = -3.5).  this is a
5 closed system simulation in kinetic reaction-progress mode.
6
7 all minerals are allowed to precipitate.
8
9 this is a test input for eq6 with the nffg option.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
*
-----
31 nmodl1= 2
32 tempc0= 25.      jtemp= 0
33 tk1= 0.      tk2= 0.      tk3= 0.
34 zistrt= 0.      zimax= 1.
35 tstrt= 0.      timemx= 1.e+8
36 kstpmx= 500      cplim= 0.
37 dzipr= 1.e+5      dzprlg= 0.5
38 ifile= 60
39 iopt1-10= 1 0 0 0 0 0 0 0 0 0
40 11-20= 0 0
41 iopr1-10= 0 0 0 0 0 0 0 1 0 0
42 iodb1-10= 0 0 0 0 0 0 0 0 0 0
43 11-20= 0 0
44 nxopt= 0
*
-----
* note fixed-fugacity inputs
*
```

```

45      nffg=      1
46      species=   co2(g)           moffg=    0.5           xlkffg=   -3.5
*
*-----
47      nrct=      1
*-----
48      reactant=   low albite
49      jcode=      0              jreac=    0
50      morr=       1.0            modr=      0.
51      nsk=        0              sk=       100000.          fk=        0.
52      nrk=        1
53      imech=      1
54      rk=         3.7e-17        ndact=    0              csigma=      1.
*-----
55      dlzidp=      0.
56      tolbt=       0.          told1=      0.          tolx=        0.
57      tolsat=      0.          tolsst=      0.
58      screw1=      0.          screw2=      0.          screw3=      0.
59      screw4=      0.          screw5=      0.
60      zklogu=      0.          zklogl=      0.
61      dlzmx1=      0.          dlzmx2=      0.
62      input file name: idw01a      revised 03/05/84
63
64      solution of distilled water to use with albite
65      dissolution experiments. the aqueous solution contains trace
66      amounts of the albite components.
67
68      ph is calculated from electrical balance
69
70      the solution is open to the atmosphere and in equilibrium with
71      atmospheric co2 levels
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92      uacion= na+
93      tempci= 2.500000e+01
94      nxmod= 1

```

```

95  species= pd-oxyannite
96      type= 1              option= -1              xlkmod= 0.
97      kct= 6              kmt= 9              kxt= 9
98      kdim= 9              kprs= 0
99      o                    5.550986244366368e+01
100     na                   1.0000000000000019e-20
101     al                   1.0000000000000024e-20
102     si                   1.0000000000000010e-20
103     h                    1.110186205346818e+02
104     c                    1.245517053099620e-05
105     electr               -8.131516293641283e-20
106     h2o                  h2o                    1.744365733541414e+00
107     na+                  na+                    -2.00000000000059913e+01
108     al+++                al+++                  -2.112188455925639e+01
109     sio2(aq)             sio2(aq)              -2.0000005430412318e+01
110     h+                   h+                    -5.666012679251850e+00
111     hco3-               co3--                  -5.666996400586441e+00
112     o2(g)               o2(g)                  -6.799999999999997e-01
113     xisteq              -2.0000000000000000e+01
114     xi                   -5.666003179937974e+00

```

---



## Appendix D. Subroutine NLKFFG Listing

This new subroutine, NLKFFG, sets up the fixed-fugacity option. Note that the common block /NF/ is also new and must appear in the MAIN program and in all of the modified subroutines in the text.

```

c nlkffg
  subroutine nlkffg(unm1,unm2,moles,xlf,nerr)
c
c   this routine sets up a fictive mineral for fixing the fugacity
c   of a specified gas.  the fugacity is fixed only if the fictive
c   mineral is in equilibrium with the aqueous system.  otherwise,
c   the fugacity may be less than the specified fixed fugacity
c   at the specified value.
c
c   unm1, unm2 = name of the gas
c   moles = number of moles of the gas to add to the system
c   xlf = log fugacity that is desired
c
  implicit logical(q),real(l,m),integer(u)
c
c7600 level 2, cdrm,cdrg,cemn,cegs,cdgmt,cdrgt,cscale
  common /ac/ cdrm(42,275),cdrg(42,15),cemn(40,275),cegs(40,15),
  $ cdmgt(275),cdrgt(15),cscale(275)
  common /dlm/ nctmax,nstmax,nrstmx,nmtmax,nxtmax,iktmax,ngtmax
c7600 level 2, uspec,umin,ugas,usolx,uelem,uoxide
  common /gg/ uspec(3,300),umin(3,275),ugas(3,15),
  $ usolx(3,20),uelem(41),uoxide(40)
c7600 level 2, ac2,awo,ars,amn,ags
  common /kg/ ac2(4,5),awo(4,5),ars(259,5),amn(275,5),ags(15,5)
  common /mt/ mte(40),mtes(40),electr,qnochb
  common /ni/ nct,nsb,nsb1,nsq,nsq1,nst,nrst,nmt,nxt,ngt,
  $ nst1,nctd,nsqd
c7600 level 2, mwtss,mwtmn,mwtgs,atwt
  common /oo/ mwtss(300),mwtmn(275),mwtgs(15),atwt(40)
c7600 level 2, vmin0,volmn,volxx
  common /un/ noutpt,npkup,ndata2,ndata3,ntabls,nahv
  common /vm/ vmin0(275),volmn(275),volxx(20)
c
  data ufix/"fix  " /
c
  nerr=0
c
  do 3162 ng=1,ngt
c   search for name in ugas
    if (unm1.ne.ugas(1,ng)) go to 3162
    if (unm2.ne.ugas(2,ng)) go to 3162
    go to 3164
  3162 continue
c   error, no match found
  write (noutpt,3171) unm1,unm2
  3171 format (/1x,2a6," has bad gas species name ")
  nerr=nerr+1
  go to 3165

```

```

c
c      load data2 variables
c
3164 nmt=nmt+1
      if (nmt .le. nmtmax) go to 3159
      write (noutpt,3176)nmtmax
3176 format (/1x,"the maximum ",i3," pure minerals have been exceeded
      $ by adding fixed fugacity species.")
      nerr=nerr+1
      go to 3165
3159 umin(1,nmt)=ufix
      umin(2,nmt)=unm1
      umin(3,nmt)=unm2
c
      dm=moles
      do 3166 nc=1,nct
      cdum=cegs(nc,ng)
      cemn(nc,nmt)=cdum
      mte(nc)=mte(nc)+cdum*dm
      mtes(nc)=mte(nc)
3166 continue
c
      mwtn(nmt)=mwtns(ng)
c
      insert zero volumes
      vmin0(nmt)=0.
c
      cdrm(nsqr1,nmt)=cdrg(nsqr1,ng)
      cdrmt(nmt)=cdrgt(ng)
      cdum2=0.
      do 3153 nc=1,nsb
      cdum1=cdrg(nc,ng)
      cdrm(nc,nmt)=cdum1
      cdum2=cdum2+abs(cdum1)
3153 continue
      cscale(nmt)=cdum2
c
c      load data3 variables
c
      do 3012 j=1,5
      amn(nmt,j)=ags(ng,j)
3012 continue
c
      alter logk values of fixed fugacity solid
      amn(nmt,1)=amn(nmt,1)+xlf
3165 continue
      return
      end

```